



Catalytic wet air oxidation of N,N-dimethylformamide aqueous solutions: Deactivation of TiO₂ and ZrO₂-supported noble metal catalysts

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ABSTRACT

N,N-dimethylformamide (DMF) is largely used as versatile solvent in various processes. It is thus present in large quantities in many industrial effluents. Oxidation of aqueous solutions of DMF with air was conducted at 180–230 °C under 50–70 bar total pressure in a batch reactor, in the absence or in the presence of heterogeneous noble metal catalysts (platinum, palladium, and ruthenium) supported on TiO₂ or ZrO₂. Under the examined reaction conditions, DMF decomposition and oxidation produced dimethylamine (DMA), methylamine (MA), and ammonium as the major N-containing products. Formic acid was also intermediately formed from the scission of the C–N bond. Nitrites and nitrates were only present in very low amounts. The addition of a catalyst accelerated the initial rates of DMF and TOC (total organic carbon) conversions, but the selectivity to N₂ was low. The production of DMA and MA was demonstrated to be very much detrimental to the chemical stability of these catalysts. A dramatic leaching of the noble metals occurred because of the complexation with the free lone pair electrons on the nitrogen atom of these amines.

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1. Introduction

Wet air oxidation is a process that might be used for the mineralization of organic pollutants in water. It consists in an oxidation at elevated temperature (150–320 °C) under high air or pure oxygen pressure (5–200 bar) and it is suitable for the treatment of aqueous effluents which cannot be treated biologically or which are too diluted for incineration [1–4].

N,N-dimethylformamide (DMF) is a powerful polar aprotic solvent which has the ability to dissolve a wide variety of organics, inorganics and resins and it has a relatively low vapour pressure [5]. Therefore, DMF is commonly used in the production of a wide range of organic chemicals and polymers, including polyurethane synthetic leather, dyes, pharmaceuticals, pesticides, polyimide resins, synthetic fibres, and polymeric membranes. It is also used as an extraction agent in the petrochemical industry. The global production of DMF was estimated at ca. 270,000 tonnes per year in 1994 [5] and there has been since an increasing demand in the production. Since it is miscible in all proportions with water and because it is extensively used in the industry, DMF is commonly found in high concentrations in many industrial wastewaters [6]. DMF is also known to have adverse impacts on the environment and the health [7,8]. Once rejected to the environment, it is found

to be highly stable and resistant to photochemical decompositions [9]. It only undergoes a slow biodegradation, even though specific DMF-degrading bacterial strains could be isolated and characterized [10–13] and it rapidly reaches inhibitory concentrations for conventional wastewater treatment plants.

In the view of its frequent occurrence in industrial wastewaters and because it is toxic and hardly biodegradable, the development of new technologies to eliminate DMF is gaining more and more attention. In many cases, when its concentration is high, DMF can be partially or totally recovered from the wastewater by distillation. However, in such a process large volumes of water must be evaporated, since DMF has the highest boiling point and the energy consumption is high [14]. In other cases, DMF-containing wastes are treated via incineration.

Hydrothermal oxidation technologies might be implemented to convert a maximum of the nitrogen in DMF to harmless N₂ (minimization of NH₄⁺, NO₃[−] and NO₂[−]) and simultaneously convert carbon to CO₂. The destruction of DMF (ca. 8.4 mM) to benign compounds has been investigated under supercritical conditions (*T* > 374 °C and *P* > 220 bar) using hydrogen peroxide as the oxidant in a continuous plug flow reactor [15]. The intermediates identified by GC–MS were trimethylamine (TMA), dimethylamine (DMA), methylamine (MA) and methanol. The oxidation of such amines was also studied under supercritical conditions by Benjamin and Savage [16,17] and Li and Oshima [18,19], using air as the oxidant.

Such wastewaters should also be effectively treated under subcritical conditions in the 150–280 °C temperature range under

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10–30 bar via wet air oxidation (WAO). To reduce the severity of the operating conditions and to achieve a higher mineralization, homogeneous as well solid catalysts can be used [1–4]. The most active heterogeneous catalysts in catalytic WAO are mixtures of metal oxides (Cu, Zn, Mn, Co, Bi) or noble metal supported catalysts. The latter catalysts have been shown to be active and leaching-resistant in the oxidation of many model pollutants [20–22] and real industrial wastewaters [23,24].

Over the past decades, considerable efforts have been made to eliminate C-containing pollutants from waters. Regarding the nitrogen-containing contaminants, the studies are less numerous and most of them concentrated on the N-containing aromatic compounds (aniline, nitrophenol, and nitrobenzene) or ammonia as model compounds [25–29]. Azo-dyes were also investigated [4]. On the opposite, little information is available on catalytic studies conducted on aliphatic amines or amides. The oxidation of methyl- and dimethylamine was studied in the presence of active carbons at 195 °C under 16 bar oxygen [30]. According to the authors, the conversion of amines ranged between 25 and 45% after 2 h reaction. Noble metal-based catalysts seemed efficient in the degradation of such compounds. A Ru/Ce catalyst has been shown to catalyse the oxidation of acetamide [32]. A complex mixture of acetonitrile, DMF and carbamide was oxidised at 160–260 °C under 20–40 bar O₂ in the presence of several solid catalysts [33]. Total conversion of carbamide was achieved after 1 h using a Ru/graphite-like carbon at 120–240 °C under 10 bar oxygen partial pressure with selectivity to N₂ of 70%. A 3 wt.% Ru catalyst supported on high-surface area zirconia was tested in the oxidation of 2.61 g L⁻¹ DMF solutions [34]. Nearly complete DMF conversion was claimed, with 88% selectivity to N₂.

We have evaluated the possibility to depollute an effluent from a manufacture of polymeric membranes, containing both glycerol and DMF, using CWAO in the presence of noble metal supported catalysts. In this study, we describe the experiments performed on DMF aqueous solutions.

2. Experimental

2.1. Catalyst preparation and characterization

For the preparation of the catalysts, commercial TiO₂ (DT51 from Millenium, anatase, 92 m² g⁻¹) and ZrO₂ supports (Mel Chemicals, monoclinic, 90 m² g⁻¹) were used. Both supports are mesoporous, with a mean pore size of 9 nm. They are known to be leaching-resistant materials under the applied reaction conditions. Catalysts containing 3 wt.% of metal (Pt, Ru, Pd) were prepared by incipient-wetness impregnation using aqueous solutions of H₂PtCl₆, Ru(NO)(NO₃)₃ or Pd(NH₃)₄(NO₃)₂. After drying overnight at 110 °C, the reduction was carried out under flowing H₂ (30 mL min⁻¹) at 300 °C for 2 h. Finally, the catalyst was flushed with Ar, passivated under 1%O₂/N₂ at room temperature and finally stored under argon.

The specific surface area of the samples was obtained from nitrogen adsorption measurements performed in a static volumetric apparatus (Micromeritics ASAP 2010). XRD characterizations were performed using a Siemens D5005 diffractometer with Cu K α radiation at 0.154184 nm. Transmission electron microscopy (TEM) direct observations were carried out on a JEOL 2010 microscope (200 kV, resolution 0.19 nm). The metal leaching was evidenced via ICP-OES analysis (inductively coupled plasma-optical emission spectroscopy) on the final mixtures (Activa, Horiba JOBIN YVON).

2.2. Catalytic oxidation experiments

All chemicals were commercial ones and analytical grade. DMF (>99.9%) was purchased from Aldrich. Dimethylamine (DMA) and

methylamine (MA) feed solutions were prepared by dilution of 40 wt% aqueous solutions purchased from Fluka. Deionised water was used to prepare all solutions.

Catalytic wet air oxidation experiments were performed in a 300 mL batch reactor made of Hastelloy, described elsewhere [23,24]. It is equipped with a magnetically driven stirrer set at 1200 rpm to avoid any mass transfer limitations of air in the aqueous phase. Temperature was maintained constant with an electronic controller. 150 mL of an aqueous solution containing 68.4 mmol L⁻¹ DMF (5 g L⁻¹) or DMA or MA, and 0.5 g catalyst were introduced into the reactor. After purging under argon to remove any trace of air, the reactor was heated to the desired reaction temperature. Air was injected in the reactor up to the predefined pressure. This time was considered to be zero time for the reaction. The liquids samples, withdrawn at different time intervals, were centrifuged at 1100 g and filtered through a 0.45 μ m membrane filter. The last liquid sample was withdrawn after the reactor was rapidly cooled down. Since no difference was observed between the last two samples at the reaction temperature and after cooling, we could conclude that no volatile compound was present in the gas phase in significant amount. This point will not be further discussed. Furthermore, after the sampling, some air was introduced again to maintain the pressure constant.

2.3. Analysis

Under our experimental conditions, dimethylamine (DMA), methylamine (MA), formic acid and ammonium ions were the dominant products. Nitrites and nitrates were produced as relatively minor products.

DMF and carboxylic acids concentrations were determined by HPLC on a ICsep Coregel 107H column with a 0.005N H₂SO₄ solution as the mobile phase (0.5 mL min⁻¹) using a refractive index detector. All products were identified based on their retention times compared to commercial compounds. DMA, MA, ammonium, nitrite and nitrate ions were analysed, after dilution by a factor of 10, using high performance ionic chromatography (HPIC, Dionex) equipped with cationic (CS16) and anionic (AS14A) columns. The eluents (1.1 mL min⁻¹) were H₂SO₄ 11 mM for cations and (Na₂CO₃ 8 mM + NaHCO₃ 1 mM) for anions.

The total organic carbon (TOC) and total nitrogen (TN) analysis were carried out on a TOC-VCSH analyser coupled with a TN unit (TNM-1) from Shimadzu. The inorganic carbon is converted to CO₂ by addition of HCl and purged using air. The non-purgeable TOC is then burnt in a catalytic oven at 680 °C and the CO₂ which is produced is quantified via an IR detector. The TN which represents the total amount of nitrogen in the liquid phase includes DMF, DMA, MA, ammonium, nitrate and nitrite. It was measured using a NO₂-specific chemiluminescence detector. The amount of CO₂ and N₂ produced may be calculated from the difference between the amount of C and N introduced as DMF and the TOC and TN measured in the liquid phase at any time, respectively. Furthermore, the carbon and nitrogen mass balances could be verified from the comparison between the HPLC, HPIC and TOC–TN analysis in order to ascertain that all intermediate and final products were correctly identified and quantified.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the XRD patterns of the TiO₂ and ZrO₂-supported Pt, Pd and Ru catalysts. The support ZrO₂ appeared to be essentially monoclinic, with a very little cubic phase. In turn, TiO₂ was pure anatase. No diffraction peak characteristic of the Ru and Pt

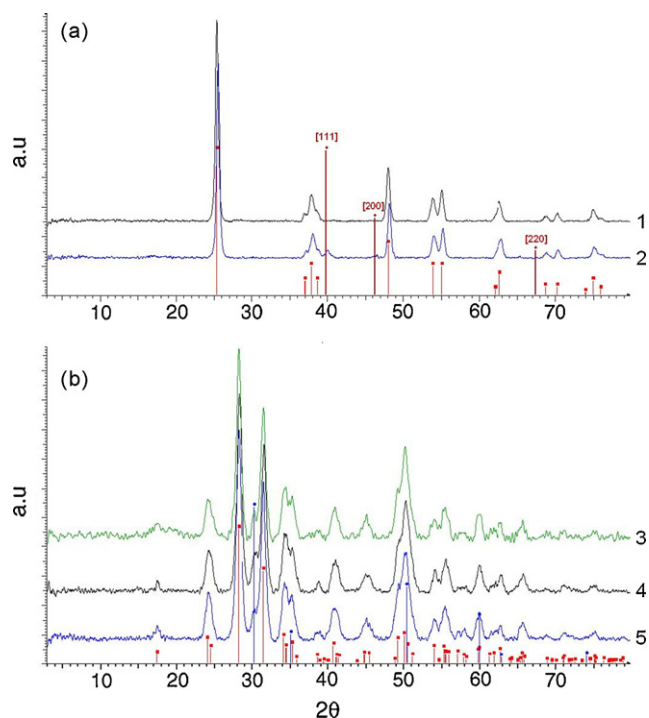


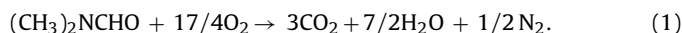
Fig. 1. XRD patterns of Pt and Ru catalysts: (a) 3%Pt/TiO₂ (1) and 3%Ru/TiO₂ (2), lines show diffraction peaks of anatase, indexed lines correspond to the platinum phase. (b) 3%Pd/ZrO₂ (3) and 3%Pt/ZrO₂ (4), 3%Ru/ZrO₂ (5), lines show diffraction peaks of monoclinic zirconia and some cubic zirconia.

phases could be observed in the 3%Ru/ZrO₂, 3%Ru/TiO₂, 3%Pd/ZrO₂ and 3%Pt/ZrO₂ catalysts, indicating that the Ru, Pd and Pt particles are probably well dispersed on the supports. TEM observations of the Ru catalysts [35] showed that such catalysts consist of small and homogeneously dispersed ruthenium particles with a mean particle size ca. 2.5 nm. On the opposite, diffraction peaks characteristic of the Pt phase could be detected on the 3%Pt/TiO₂ catalyst. Representative TEM micrographs of this catalyst are shown in Fig. 2. The distribution of the Pt particles is a bit larger (1.5–5 nm) and some larger particles are also observed, in agreement with the XRD results.

3.2. Non-catalytic thermal wet air oxidation of DMF: effect of temperature

A series of non-catalytic experiments were carried out at different temperatures and pressures (180–230 °C, 50–70 bar of total

pressure). In addition to the removal of DMF as a function of time, Fig. 3 also presents the evolutions of (i) the yields in the different nitrogen species (DMA, MA, NH₄⁺) and (ii) the concentration of formic acid for the reactions performed at 180, 210 and 230 °C under 70 bar total pressure. The amount of oxygen available in the reactor (10.2, 8.8, and 8.0 g L⁻¹) accounts for 110, 95 and 86% amounts of the stoichiometric concentration to achieve the complete oxidation of DMF in CO₂, N₂ and H₂O, respectively, according to Eq. (1).



The NO₂⁻ and NO₃⁻ concentrations are not shown since they are always lower than 0.4 and 3 mmol L⁻¹, respectively.

Upon heating under argon, DMF got degraded. Degradation increased with temperature and accounted for 20% of the DMF conversion at time zero at 230 °C. Dimethylamine (DMA) and formic acid were subsequently formed in nearly equivalent concentrations, suggesting that the scission of the C–N bond of the amide was the main reaction.

This initial conversion was mainly attributed to the thermal decomposition of DMF. Indeed, in an experiment conducted under argon and the autogeneous pressure of water at 180 °C, 56% DMF thermal hydrolysis was observed after 6 h. DMA and formic acid were formed in comparable concentrations without any significant TOC conversion. Only traces of MA and NH₄⁺, which remained stable under these reaction conditions, were detected.

Under air pressure, DMF was further eliminated, at different rates depending on the temperature. This conversion yielded DMA and formic acid which reacted further. The degree of DMF removal was higher than under inert atmosphere, indicating that some degradation of DMF by oxygen also occurred, simultaneously with the thermal degradation. This observation is in accordance with Imamura's results [31] who noted, in the wet air oxidation of different amides (formamide, N-substituted formamides, N-unsubstituted amides with different molecular weights, etc), that amides decomposed via two competitive mechanisms: (i) the thermal cleavage of the C–N bond, followed by the oxidation of the resulting amine and acid fragments, and (ii) the direct reaction of oxygen with the amides. The direct attack of oxygen on the amides was correlated with the carbon content in the molecule, i.e. it was more and more important as the molecular weight increased.

During the reaction with DMF under air, DMA was intermediately produced as expected and, the maximum yield in DMA was shifted towards shorter reaction times as the reaction temperature increased. Methylamine (MA), ammonium and nitrates were formed from the DMA oxidation. MA reached a maximum, and

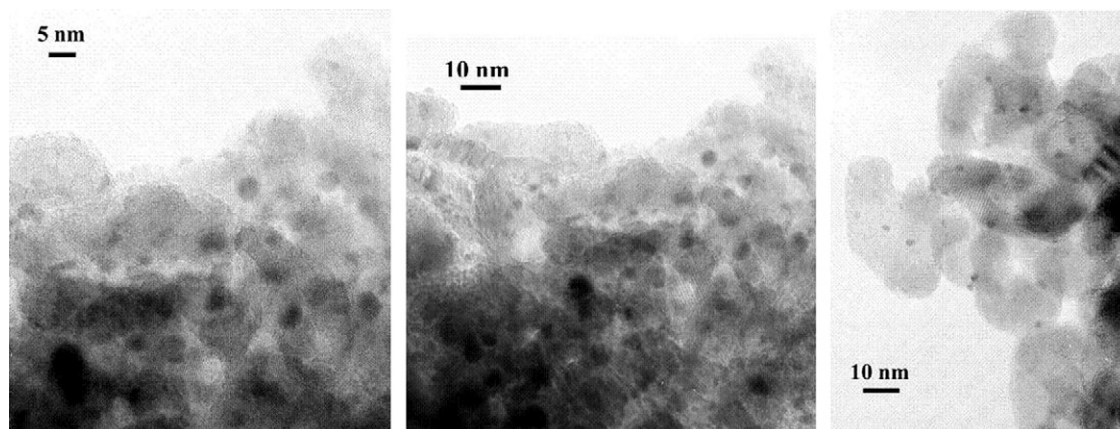


Fig. 2. Representative TEM micrographs of the 3%Pt/TiO₂ catalyst.

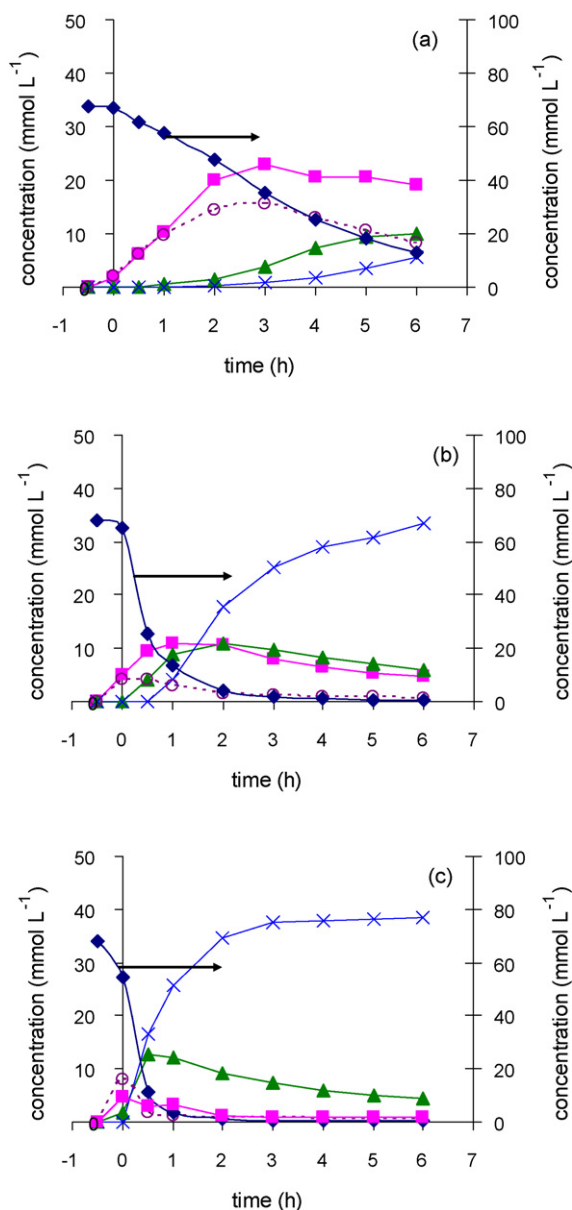


Fig. 3. Non-catalytic wet air oxidation of DMF aqueous solutions (150 mL, 5 g L⁻¹, 68.4 mmol L⁻¹) at different temperatures under 70 bar total pressure: (a) 180 °C, (b) 210 °C and (c) 230 °C. (◆) DMF, (■) DMA, (▲) MA, (×) NH₄⁺, and (○) formic acid.

then decreased as the reaction proceeded, whereas NH₄⁺ accumulated. In all experiments, only traces of nitrites (<0.4 mmol L⁻¹ maximum) were detected. Formic acid also formed from the C–N scission and it was easily more and more oxidised to carbon dioxide and water as the temperature increased. Thus, in the absence of any catalyst, a temperature of at least 230 °C was required to reach significant conversions of DMA, MA and formic acid. However, even at such high temperature the reactivity of amines, DMA and especially MA, was rather low. After 6 h reaction at 230 °C the conversion of DMF was nearly complete and the product distribution based on the initial DMF concentration was 2.3% DMA, 6.3% MA, 56.8% NH₄⁺, 0.15% NO₂⁻, and 3.75% NO₃⁻. The balance for nitrogen (30.7%) was assumed to be molecular nitrogen, according to experimental results already presented in the literature [26–28]. These publications also indicated that only traces of NO_x were sometimes detected in the gas phase. Furthermore, in the absence of any catalyst, NH₄⁺ appeared as a refractory product accumulating in the reaction as the reaction proceeded. Indeed, ammonium was the

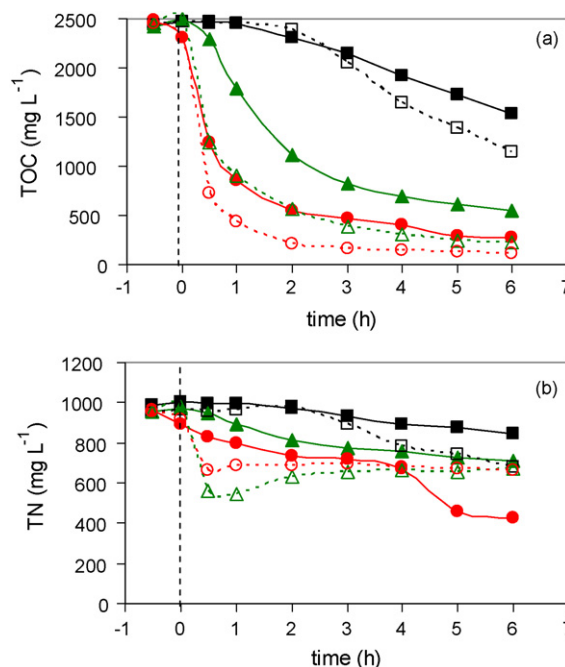


Fig. 4. TOC (a) and TN (b) evolutions upon non-catalytic oxidation reactions of DMF aqueous solution (150 mL, 5 g L⁻¹, 68.4 mmol L⁻¹) at different temperatures under 70 bar total pressure. (■, □) 180 °C, (▲, △) 210 °C and (●, ○) 230 °C, closed symbols: as measured, open symbols: as calculated.

dominant N-containing product formed at 210 and 230 °C, and it remained very stable under these operating conditions.

Fig. 4 shows the evolutions of the TOC and TN concentrations during the same experiments in the absence of any catalyst at the different temperatures.

The TOC conversion proceeded rather slowly at 180 °C (38% after 6 h). As temperature increased to 210 and 230 °C, the TOC conversion became significant and reached 78 and 89%, respectively (after 6 h reaction). On the other hand, the TN conversion was low at any temperature (13, 19, and 55%, respectively) since refractory intermediates were formed.

Next, having identified and quantified the reaction products, the measured TOC and the “theoretical” TOC, calculated from the chromatographic analysis for DMF, DMA, MA and formic acid were compared (Fig. 4a). The same comparisons were made between the measured TN values and the TN values calculated from the concentrations of DMF, DMA, MA + NH₄⁺, NO₃⁻ and NO₂⁻ (Fig. 4b).

The agreement between TOC values was satisfying at the beginning of the reaction. However, mass balances deviated from $t=3$ h at 180 °C and from $t=0.5$ h at 210 and 230 °C. This deviation was maintained for the rest of the reaction. We considered these discrepancies could be due to the formation of undetectable compounds using the chromatographic setup we used. By comparison with the results presented in Fig. 3, we could notice that this phenomenon was somehow related to the conversion of DMA. Some results from the literature on the supercritical oxidation of DMA revealed the existence of methanol as a minor product [17,18]. However, MeOH was not detected in our samples. The same authors also mentioned about an unidentified product that they considered to be formaldehyde.

In the case of nitrogen, the measured and calculated TN values did not fit well. Though important uncertainties were associated to the high dilution levels required before the ionic chromatography analysis, the existence of unidentified compounds cannot be excluded. Furthermore, to verify if some amines or ammonia could be stripped in the gas phase during the reaction, analysis was also

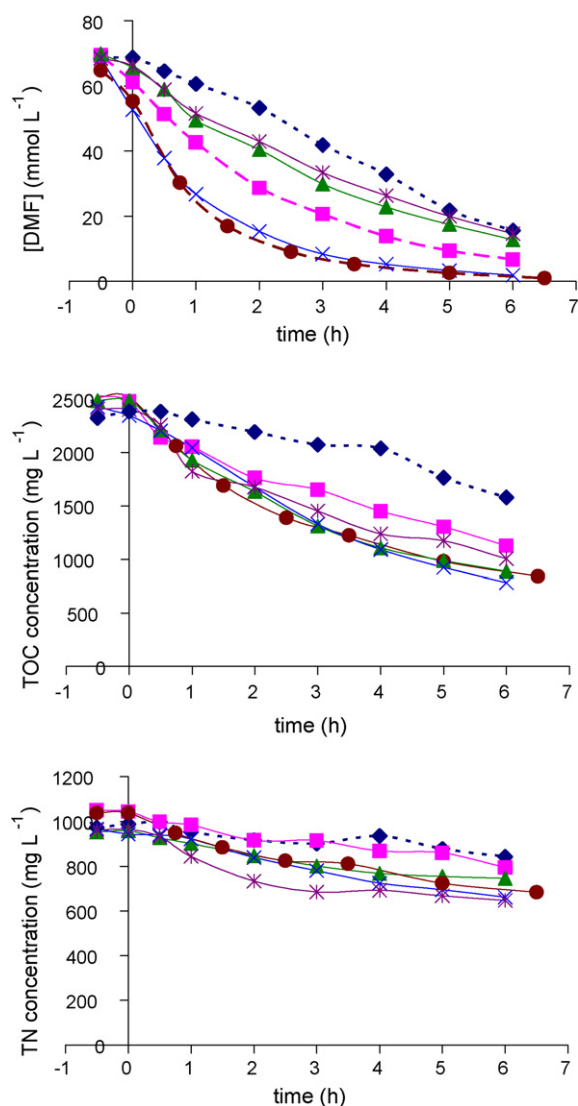


Fig. 5. DMF catalytic oxidation at 180 °C under 50 bar in the absence or in the presence of different catalysts. (♦) No catalyst, (■) Pt/ZrO₂, (▲) Pd/ZrO₂, (×) Ru/TiO₂, (*) Ru/ZrO₂, and (●) Pt/TiO₂.

performed after the reactor was cooled down. No significant difference was observed that could explain the deficiency in nitrogen and carbon mass balances.

The effect of the air pressure (50 and 70 bar) was examined at 180 °C. At this temperature under 50 bar, the concentration of oxygen was close to the stoichiometric concentration required for the total mineralization of DMF. Very similar results were obtained as far as the TOC and TN conversions and the evolutions of the N-base and C-base products are concerned.

The addition of the ZrO₂ support used as a support for the preparation of the Pt and Ru catalysts did not significantly change the results obtained at 180 °C in the absence of any catalyst. The DMF and TOC conversions were slightly higher after 6 h: 90% vs. 77% and 43% vs. 36%, respectively. In conclusion, the support showed only little activity in this reaction.

3.3. Catalytic DMF oxidation

Platinum, palladium and ruthenium supported catalysts were examined in the oxidation of DMF at 180 °C under 50 bar total pressure. Fig. 5 compares the evolutions of the DMF, TOC and TN concentrations as a function of time.

As reported in the first part of this manuscript, DMF thermal degradation is important in the absence of catalyst. With the introduction of a catalyst, the disappearance of DMF is even faster but occurs to different extents depending on the catalyst. The catalysts supported on TiO₂ (Pt/TiO₂ and Ru/TiO₂) were the most active. This could be related to a support effect even though both supports show the same specific surface area and porosity. However, the bare TiO₂ support was not tested while its higher surface acidity (PZC, pH at point of zero charge 4.4) could be responsible for this even stronger promoting effect compared to ZrO₂ (PZC 6.1).

The initial TOC abatement rates were also significantly higher in the presence of a catalyst, demonstrating some activity of the catalysts in the oxidation of DMF or the intermediate products. However, this effect was not as large as expected. TOC conversions after 6 h ranged from 50 to 73% compared to 38% in the non-catalysed reaction.

In addition, the total nitrogen abatements are in the range 17–33%, to be compared to 13% in the absence of catalyst. These higher abatements may be attributed to the catalytic conversion of the N-species to molecular nitrogen in the presence of the catalysts. The distribution of the nitrogen-containing compounds was further examined in more details. Fig. 6 shows the product distributions as a function of time in the presence of the ZrO₂-supported Pt, Pd and Ru catalysts.

At a given temperature, the presence of the catalyst modified the distribution of the N-containing compounds compared to the non-catalysed experiment (Fig. 1a). Pd and Ru led higher DMA conversions and higher amounts of ammonium ions. At the end of the reaction, DMA represented 13–15% of the residual nitrogen and the ammonium content was 32–34%. This higher mineralization of the amines explains the higher TOC abatement obtained compared to the non-catalytic experiment. Surprisingly, the Pt catalyst behaved differently. The Pt catalyst only showed some significant activity during the first 2 h with the formation of MA and NH₄⁺. However, high concentrations of DMA remained in the reaction medium at the end of the reaction and the final selectivity to DMA and ammonium was 38 and 23%, respectively. Indeed, as we shall discuss later, a substantial fraction of the noble metals was leached in the presence of amines and this leaching was particularly important in the case of platinum catalysts.

Furthermore, formic acid was detected in very low concentration in the palladium catalysed reaction. Once formed, it was not converted in the presence of the platinum or ruthenium catalysts. Formic acid is usually highly reactive at such temperatures and its reactivity increases with the addition of noble metal supported catalysts [36]. One reason for this unusual stability could be the leaching of the active phase upon reaction. Another possible reason could be the pH of the reaction medium which became alkaline upon formation of DMA. Formic acid is then present as a formate, which is less reactive.

TN balance was relatively good, whereas the same trend as in the absence of catalyst was observed for the TOC balance. This is illustrated in Fig. 7 which gives the carbon and nitrogen balances upon DMF oxidation in the presence of 3%Ru/TiO₂.

This observation tends to indicate that the unidentified compounds do not contain much nitrogen.

3.4. Catalytic DMA and MA oxidation

Dimethylamine and methylamine are the amines which are formed during the degradation of DMF. In order to better understand the oxidation mechanism of DMF, the non-catalytic and catalytic wet air oxidation of DMA and MA was studied at 180 °C under 50 bar total pressure in the absence or in the presence of 0.5 g of catalyst, using 68.4 mmol L⁻¹ DMA or MA aqueous solutions. First, the reactivity of DMA under 50 bar of argon was investigated.

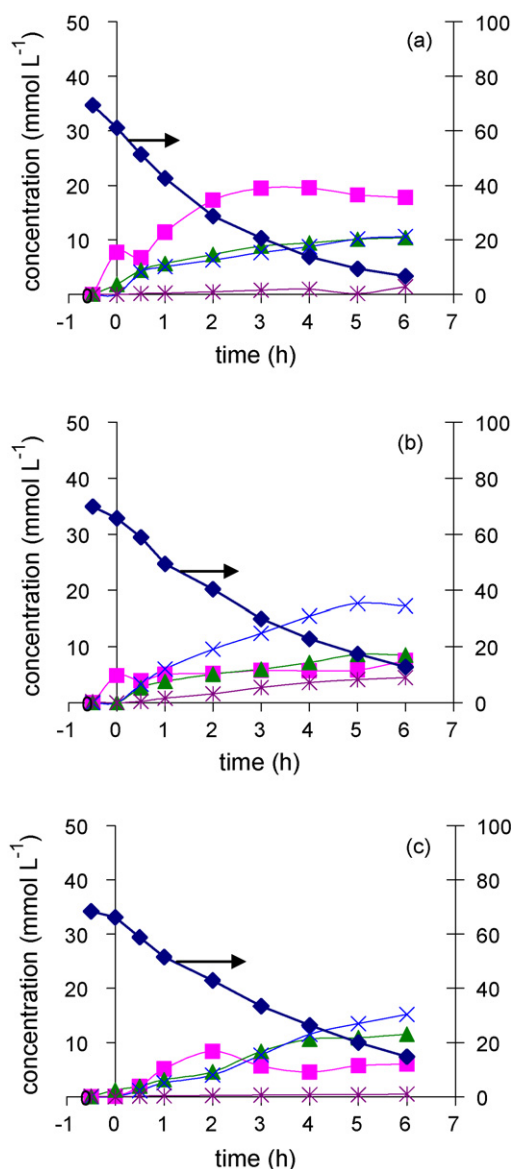


Fig. 6. Evolution of (◆) DMF, (■) DMA, (▲) MA, (×) NH_4^+ , and (*) NO_3^- concentrations as a function of time upon DMF CWAQ at 180 °C under 50 bar total pressure in the presence of (a) Pt/ZrO₂, (b) Pd/ZrO₂, and (c) Ru/ZrO₂.

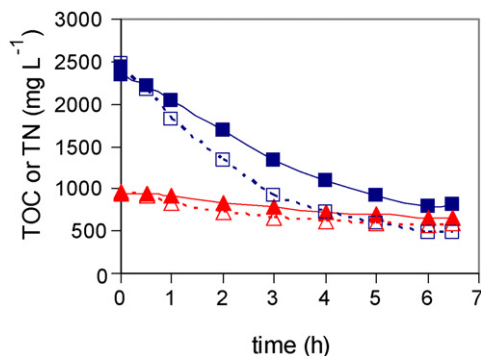


Fig. 7. Carbon (■, □) and nitrogen (▲, △) mass balances during oxidation of DMF aqueous solutions in the presence of 3% Ru/TiO₂ (150 mL, 5 g L⁻¹, 68.4 mmol L⁻¹, 180 °C under 50 bar total pressure). Closed symbols: as measured, open symbols: as calculated.

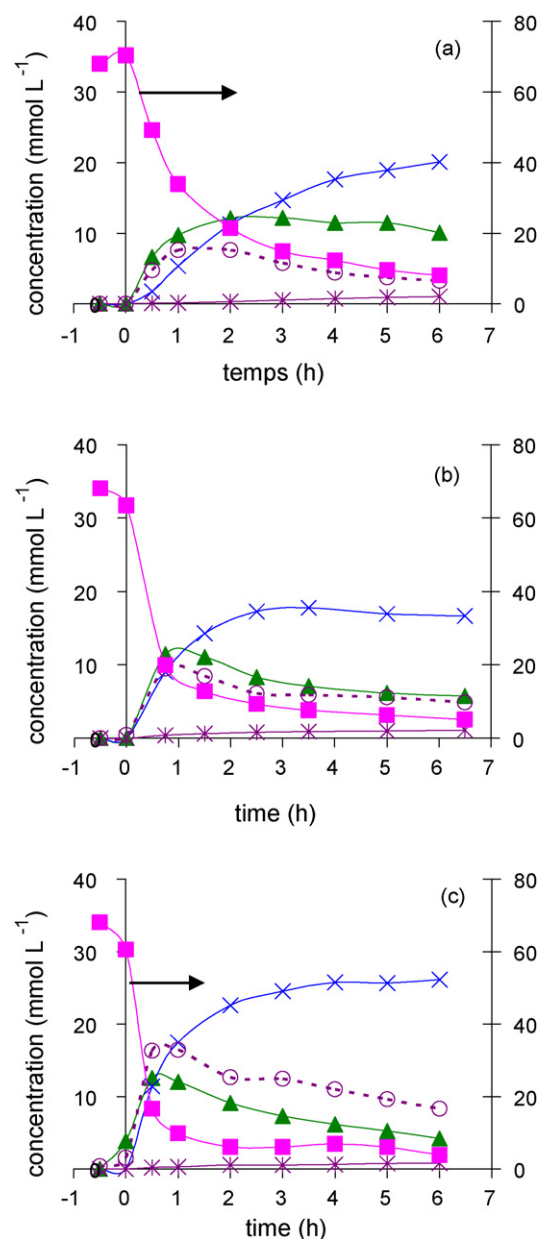


Fig. 8. Oxidation of 68.4 mmol L⁻¹ aqueous solutions of DMA (150 mL, TOC = 1642 mg L⁻¹) at 180 °C under 50 bar: (a) in the absence of a catalyst, (b) in the presence of Pt/TiO₂, and (c) in the presence of Ru/TiO₂. (■) DMA, (▲) MA, (×) NH_4^+ , (*) NO_3^- and (○) formic acid.

Under these conditions, thermal degradation was very limited, suggesting that the cleavage of the C–N bond does not occur to a significant extent (as the initial DMA degradation step).

Fig. 8 illustrates the results obtained in the absence (Fig. 8a) or in the presence of TiO₂-supported platinum and ruthenium catalysts (Fig. 8b and c). The ZrO₂-supported catalysts behaved similarly in the oxidation of DMA (not shown).

In our study, in the absence of catalyst (Fig. 8a), the DMA conversion in air at 180 °C was as high as 89% after 6 h while Aguilar et al. [30] did not observe any decomposition of DMA or MA (1000 ppm) at 195 °C as monitored via acid–base titration using a pH indicator. As previously observed upon DMF oxidation, DMA was primarily oxidised to MA and formic acid. Indeed, the initial slope of the NH_4^+ curve was zero, indicating that ammonium is only formed as a secondary product. The yield in N₂, estimated from the difference between the initial concentration of DMA and the total concen-

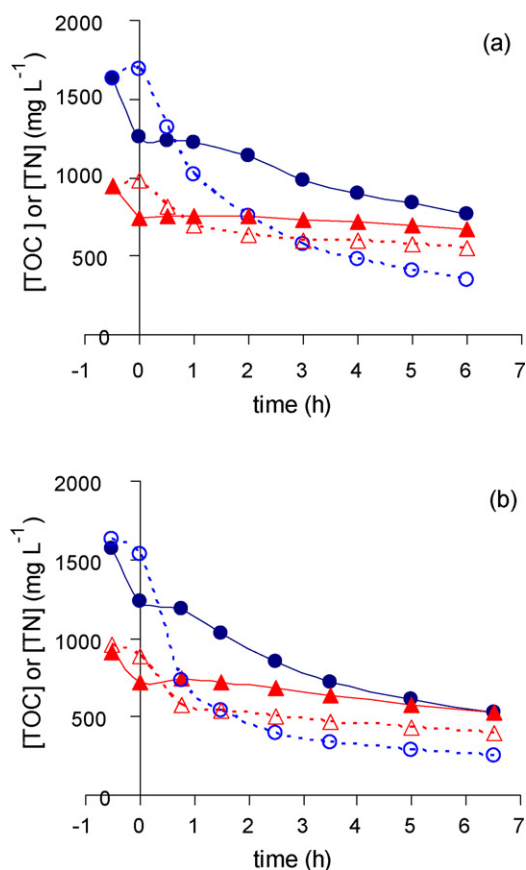


Fig. 9. Carbon (●, ○) and nitrogen (▲, △) mass balances in the liquid phase upon oxidation of DMA aqueous solutions: (a) in the absence of catalyst and (b) in the presence of Pt/TiO₂. Closed symbols: as measured, open symbols: as calculated.

tration in products ($\text{MA} + \text{NH}_4^+ + \text{NO}_3^- + \text{NO}_2^-$), is very low. Fig. 8a shows almost no evolution of the TN concentration in the liquid phase during the reaction, confirming the low selectivity in N₂.

In the presence of a catalyst and during the first hour (Fig. 8b and c), the conversion of DMA was much more rapid (75 and 86% DMA conversion in the presence of Pt/TiO₂ and Ru/TiO₂, respectively). However, after 1 h, the DMA concentration levelled off. Compared to the non-catalytic run (Fig. 8a) a subsequent decrease of MA was observed in the presence of a catalyst, whereas NH₄⁺ remained stable. In all examined reaction conditions, NH₄⁺ was the dominant final product and nitrate ions were only produced in very minor quantities.

Fig. 9 shows the evolution of both carbon and nitrogen mass balances upon DMA oxidation, in the absence of catalyst or in the presence of Pt/TiO₂. The same trends were observed with Ru/TiO₂ and the ZrO₂-supported catalysts. Comparing the measured and calculated TN values, we could conclude that the major N-containing products were analysed. On the other hand, the mass balance for the carbonaceous products was never complete and the deviation increased as the DMA conversion increased. Therefore, the hypothesis we proposed for the interpretation of the results obtained upon DMF catalytic oxidation, about the production of N-free compounds from DMA, is further validated based on these results.

The last experiments were performed on MA aqueous solutions. The experimental conditions were the same as for DMA: 180 °C, 50 bar total pressure, 68.4 mmol L⁻¹ MA and 0.5 g catalyst. As observed earlier for DMA, the initial MA and TOC abatement rates increased with the addition of a catalyst, but rapidly slew down after some time. The evolution of the ammonium and formic

Table 1

Percentage of metal leaching from the solid upon reaction as measured by chemical analysis of the final treated effluents after oxidation of DMF, DMA, MA at 180 °C under 50 bar total pressure.

Substrate	Catalyst	%Ru leached	%Pt leached	%Pd leached
DMF	3%Ru/ZrO ₂	24		
	3%Ru/TiO ₂	25		
	3%Pt/ZrO ₂		55, 88, 94 ^a	
	3%Pt/TiO ₂		28	
	3%Pd/ZrO ₂			17
DMA	3%Ru/ZrO ₂	19, 35 ^a		
	3%Ru/TiO ₂	28		
	3%Pt/ZrO ₂		86, 90, 97 ^a	
	3%Pt/TiO ₂		49	
MA	3%Ru/ZrO ₂	34		
	3%Ru/TiO ₂	23		
	3%Pt/ZrO ₂		85, 103 ^a	
	3%Pt/TiO ₂		63	

^a Independent experiments.

acid formation was consistent with our prior work on DMF and DMA.

The catalysts' performances in the DMA and MA oxidations suggest some rapid deactivation of the catalyst. One possible reason could be the leaching of the active phase [37]. In the following, our attention focused on the chemical stability of the supported catalysts upon reaction.

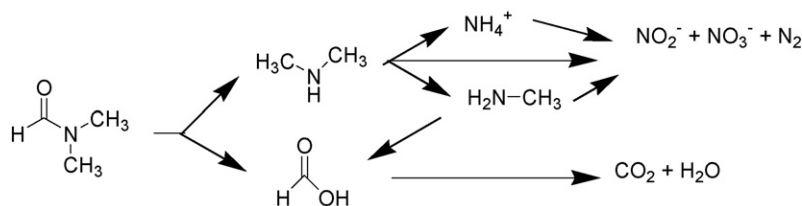
3.5. Leaching of active phase

Solutions after 6 h reaction were analysed for Pt, Ru or Pd. The results are presented in Table 1.

Surprisingly, a dramatic leaching of the metallic phase was observed for all catalysts, whereas no Ti or Zr could be detected (detection limit: 0.1 ppm). Leaching was observed upon DMF, DMA or MA oxidation, suggesting it might be attributed to the presence of amines. Leaching was very rapid and the most important for the platinum catalysts. Almost all the platinum initially present was washed out from the Pt/ZrO₂ catalyst upon reaction.

No experiments were carried out to check the possible homogeneous contribution of platinum or ruthenium after leaching of the catalysts. Such a catalytic effect may certainly be discarded, as supported by the following: (i) the observed reaction rates dramatically decreased as soon as an important leaching was detected and (ii) reactions performed at 180 °C under 50 bar total pressure on glycerol or (glycerol + DMF) aqueous solutions were compared. In the absence of any catalyst, the conversion of glycerol was negligible, whereas in the presence of 3%Ru/ZrO₂ this conversion was rapid and complete within 2 h. In the case of the (glycerol + DMF) solution, the initial glycerol disappearance rate was almost identical. However, after ca. 1 h, due to the important leaching of the catalyst, no further conversion was observed. Conversion remained at a plateau, ca. 85%, indicating there were no more catalytic sites available.

Our observations are contradictory to the results previously reported in the literature [32,33]. Indeed, these authors claimed that such catalysts were stable and highly selective to N₂ in the CWAQ of DMF under similar operating conditions. Our results demonstrated the opposite. Particularly, in the case of the Ru/ZrO₂ catalyst, the only significant difference between our work and the results from the literature is the nature of the support. Sun et al. [34] prepared a high-surface area zirconia (190 m² g⁻¹) via (i) precipitation and digestion at 190 °C for 60 h of an hydrous zirconia and (ii) calcination at 450 °C; whereas we used a commercial zirconia. Both supports were well-crystallized. The metal deposition method and the reduction protocol were the same:



Scheme 1. DMF oxidation pathways.

incipient-wetness impregnation with a Ru salt aqueous solution, drying and reduction in flowing hydrogen at 300–350 °C for 3 h. From our results, it is indeed evident that the DMF disappearance rate is initially enhanced upon the addition of a catalyst. However, after a very short period of time, DMA and MA are formed which are quite well-known as complexing agents for metals. The leaching of the active phase was consequently attributed to the presence of the lone pair electrons on the nitrogen atom which are able to create a strong chemical bond with the metal atoms.

If we now consider the investigations performed on different N-containing molecules in the presence of supported noble metal catalysts, most of them concern aniline, nitrobenzene or ammonium. In those cases, the reason why leaching was never reported, could be that aniline is mainly transformed to phenyl-hydroxylamine which is in turn rapidly converted to phenol and ammonium, or to nitrobenzene and azobenzene, which ones have no complexing ability. Similarly, ammonium ions, without any lone pair electrons, did not lead any leaching. Complexation of the metals by the amines, through the lone pair electrons on the nitrogen atom was confirmed after acidification of the reaction medium. Sulphuric acid (74 $\mu\text{mol L}^{-1}$) was added to the DMA aqueous solution to protonate the amine. As a result, leaching was strongly inhibited. However, the catalysts also lost any activity in the oxidation of the chemically modified DMA.

In summary, since an extensive leaching of the active phase was observed, performances we measured upon reaction did not reflect the real catalysts' activity all along the reaction.

3.6. Global reaction network

Based on the experimental data received upon DMF, DMA and MA oxidations, we could finally propose a set of reaction paths for the degradation of DMF upon wet air oxidation, as given in Scheme 1.

It was concluded that DMF might be thermally hydrolysed to DMA and formic acid. DMA was further converted to formic acid, MA and NH_4^+ . MA is also oxidised to NH_4^+ . Mineralization to N_2 may also occur, especially in the presence of a catalyst. Furthermore, MA and NH_4^+ might be transformed to more oxidised species such as NO_2^- and NO_3^- . The subsequent catalytic oxidation of ammonia did not occur during our experiments, because of the extensive leaching of the active phase.

4. Conclusions

This work concerned the wet air oxidation of DMF in the presence of supported Pt, Pd and Ru catalysts. Under our experimental conditions (180–230 °C, 50–70 bar total pressure), DMA and formic acid were the primary products of DMF decomposition. DMA further reacts with air to yield MA, ammonium and only small amounts of NO_3^- . Formic acid decomposed to CO_2 and water. Since DMA and MA are formed, a rapid deactivation of the catalysts was experienced. An extensive leaching of the metal, by complexation through

the lone pair electrons on the nitrogen atom, was clearly evidenced, in contrast with the results published earlier. The use of such catalysts for the elimination of amides or aliphatic amines via catalytic wet air oxidation is thus not recommended. Thus, the development of alternative methods for DMF abatement is very important. No information is presently available about other wet oxidation processes for the treatment of such effluents (WO with soluble catalysts or catalytic carbon materials, use of a Fenton system, etc).

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